

FORM PTO-1390 (REV. 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER <b>ACD2665US</b>
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (If known, see 37 CFR 1.5) <b>09/889436</b>
INTERNATIONAL APPLICATION NO. <b>PCT/EP00/00003</b>	INTERNATIONAL FILING DATE <b>6 January 2000</b>	PRIORITY DATE CLAIMED <b>12 January 1999</b>	
TITLE OF INVENTION <b>AQUEOUS PEROXIDE EMULSIONS</b>			
APPLICANT(S) FOR DO/EO/US <b>Hans Westmijze and Boen Ho O</b>			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information			
<ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.</li> <li>4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).</li> <li>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input checked="" type="checkbox"/> has been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ol> </li> <li>6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> is attached hereto.</li> <li>b. <input checked="" type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).</li> </ol> </li> <li>7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> <li>a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).</li> <li>b. <input type="checkbox"/> have been communicated by the International Bureau.</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input type="checkbox"/> have not been made and will not be made.</li> </ol> </li> <li>8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</li> <li>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <b>(unsigned) 3 pgs.</b></li> <li>10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</li> </ol>			
Items 11 to 20 below concern document(s) or information included:			
<ol style="list-style-type: none"> <li>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</li> <li>13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment.</li> <li>14. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</li> <li>15. <input type="checkbox"/> A substitute specification.</li> <li>16. <input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li>17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.</li> <li>18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).</li> <li>19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).</li> <li>20. <input checked="" type="checkbox"/> Other items or information: <ol style="list-style-type: none"> <li>1. <b>copy of International Preliminary Examination Report dated 26 October 2000</b></li> <li>2. <b>return receipt postcard</b></li> <li>3. <b>marked version of changes</b></li> </ol> </li> </ol>			
			Express Mail Label No.: <b>EM122095263US</b>

U.S. PATENT APPLICATION NO. **09/889436**INTERNATIONAL APPLICATION NO.  
**PCT/EP00/00003**

ATTORNEY'S DOCKET NUMBER

**ACD2665US**21. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**Neither international preliminary examination fee (37 CFR 1.482)  
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO  
and International Search Report not prepared by the EPO or JPO. .... \$1000.00International preliminary examination fee (37 CFR 1.482) not paid to  
USPTO but International Search Report prepared by the EPO or JPO ..... \$860.00International preliminary examination fee (37 CFR 1.482) not paid to USPTO  
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... \$710.00International preliminary examination fee (37 CFR 1.482) paid to USPTO  
but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... \$690.00International preliminary examination fee (37 CFR 1.482) paid to USPTO  
and all claims satisfied provisions of PCT Article 33(1)-(4) ..... \$100.00**ENTER APPROPRIATE BASIC FEE AMOUNT =****CALCULATIONS PTO USE ONLY**\$ **860.00**Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30  
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$ --

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$
Total claims	<b>40</b> - 20 =	<b>20</b>	x \$18.00	<b>\$360</b>
Independent claims	<b>1</b> - 3 =	--	x \$80.00	\$ --

MULTIPLE DEPENDENT CLAIM(S) (if applicable)	+ \$270.00	\$270
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**TOTAL OF ABOVE CALCULATIONS =**\$ **630**☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above  
are reduced by 1/2.

+

**SUBTOTAL =**\$ **1490**Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30  
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$ --

**TOTAL NATIONAL FEE =**\$ **1490**Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be  
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

\$ --

**TOTAL FEES ENCLOSED =**\$ **1490**Amount to be  
refunded:

\$

charged:

\$

- a. ☐ A check in the amount of \$ \_\_\_\_\_ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. **01-1350** in the amount of \$ **1490.00** to cover the above fees.  
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any  
overpayment to Deposit Account No. **01-1350**. A duplicate copy of this sheet is enclosed.
- d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card  
information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR  
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

**Richard P. Fennelly**  
**Akzo Nobel Inc.**  
**Intellectual Property Department**  
**7 Livingstone Avenue**  
**Dobbs Ferry, NY 10522-3408**  
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SIGNATURE

**Richard P. Fennelly**

NAME

**25,677**

REGISTRATION NUMBER

**July 12, 2001**

Patent

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

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In re Application of: : Docket No: ACD 2665 US  
HANS WESTMIJZE et al. :  
: Examiner: ----  
Serial No: To be Assigned :  
: Group Art Unit: ----  
Filing Date: To be Assigned :  
: Title: AQUEOUS PEROXIDE EMULSIONS :  
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PRELIMINARY AMENDMENT

Honorable Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Please amend the above-identified application as follows:

IN THE SPECIFICATION:

AMEND THE BEGINNING OF PAGE 1 SO THAT IT APPEARS AS FOLLOWS:

-- AQUEOUS PEROXIDE EMULSIONS

This application is a national phase filing of PCT/EP00/00003, filed January 6, 2000, which application claims priority from European Patent Application No. 99200066.1, filed January 12, 1999.

This invention relates to aqueous emulsions of peroxides, optionally containing an anti-freeze and/or further additives, which contain a specific emulsifier system comprising a copolymer

of an  $\alpha,\beta$ -unsaturated dicarboxylic acid and a  $C_{8-24}$   $\alpha$ -olefin the acid groups of which are esterified with an ethoxylated alcohol having a degree of ethoxylation of 1-45.--.

AMEND CLAIMS 3, 6 and 8-12 SO THAT THEY APPEAR AS FOLLOWS:

3. Emulsion according to claim 1 wherein the peroxide is selected from the group consisting of peroxyesters, peroxydicarbonates, peroxyarbonates, diacyl peroxides, peroxides, and combinations thereof, and in which said peroxide is present in an amount of 30-70% by weight, based on the weight of the emulsion.

6. Emulsion according to any one of claims 1-5 wherein the copolymer is present in an amount of 0.05 to 20% by weight and the ethoxylated fatty alcohol is present in an amount of 0.02-15% by weight, while the total weight of both compounds is at least 0.5% by weight, all based on the weight of the peroxide in said emulsion.

8. Emulsion according to any one of claims 1-5 wherein the HLB value of the ethoxylated fatty alcohol is greater than 16.5, preferably greater than 17.0.

9. Emulsion according to any one of claims 1-5 wherein the droplet size of the emulsion, when measured using a Malvern Easy Sizer, is characterized by a d50 of 0.1-2.0  $\mu\text{m}$  and a d99 of 0.5-9.0  $\mu\text{m}$ .

10. Emulsion according to any one of claims 1-5 with a viscosity of 10-300 mPa.s.

11. Use of an emulsion according to any one of claims 1-5 in a polymerization or polymer modification reaction, preferably a reaction involving the polymerization of at least vinyl chloride.

12. Polyvinyl chloride obtainable by a process involving the reaction of at least vinyl chloride monomer and a peroxide that was used in the form of an emulsion according to any one of claims 1-5.

REMARKS

Formal examination of the new Claims herein is requested in due course.

Respectfully submitted,

*Richard P. Fennelly*

Richard P. Fennelly  
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Reg. No. 25,677

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MARKED COPY OF SPECIFICATION/CLAIMS SHOWING CHANGES

IN THE SPECIFICATION (AT PAGE 1):

-- AQUEOUS PEROXIDE EMULSIONS

This application is a national phase filing of PCT/EP00/00003, filed January 6, 2000, which application claims priority from European Patent Application No. 99200066.1, filed January 12, 1999.

This invention relates to aqueous emulsions of peroxides, optionally containing an anti-freeze and/or further additives, which contain a specific emulsifier system comprising a copolymer of an  $\alpha, \beta$ -unsaturated dicarboxylic acid and a  $C_{8-24}$   $\alpha$ -olefin the acid groups of which are esterified with an ethoxylated alcohol having a degree of ethoxylation of 1-45.--.

IN THE CLAIMS:

3. Emulsion according to claim 1 [or 2] wherein the peroxide is selected from the group consisting of peroxyesters, peroxydicarbonates, peroxycarbonates, diacyl peroxides, peroxides, and combinations thereof, and in which said peroxide is present in an amount of 30-70% by weight, based on the weight of the emulsion.

6. Emulsion according to any one of [the preceding] claims 1-5 wherein the copolymer is present in an amount of 0.05 to 20% by weight and the ethoxylated fatty alcohol is present in

an amount of 0.02-15% by weight, while the total weight of both compounds is at least 0.5% by weight, all based on the weight of the peroxide in said emulsion.

8. Emulsion according to any one of [the preceding] claims 1-5 wherein the HLB value of the ethoxylated fatty alcohol is greater than 16.5, preferably greater than 17.0.

9. Emulsion according to any one of [the preceding] claims 1-5 wherein the droplet size of the emulsion, when measured using a Malvern Easy Sizer, is characterized by a d50 of 0.1-2.0  $\mu\text{m}$  and a d99 of 0.5-9.0  $\mu\text{m}$ .

10. Emulsion according to any one of [the preceding] claims 1-5 with a viscosity of 10-300 mPa.s.

11. Use of an emulsion according to any one of [the preceding] claims 1-5 in a polymerization or polymer modification reaction, preferably a reaction involving the polymerization of at least vinyl chloride.

12. Polyvinyl chloride obtainable by a process involving the reaction of at least vinyl chloride monomer and a peroxide that was used in the form of an emulsion according to any one of claims [1-10] 1-5.

AQUEOUS PEROXIDE EMULSIONS

5 This invention relates to aqueous emulsions of peroxides, optionally containing an anti-freeze and/or further additives, which contain a specific emulsifier system comprising a copolymer of an  $\alpha,\beta$ -unsaturated dicarboxylic acid and a  $C_{8-24}$   $\alpha$ -olefin the acid groups of which are esterified with an ethoxylated alcohol having a degree of ethoxylation of 1-45.

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Such peroxide emulsions are known from, for instance, EP-A-0 492 712. In this patent application it is disclosed in Examples 14-18 how the copolymer of an  $\alpha,\beta$ -unsaturated dicarboxylic acid and a  $C_{8-24}$   $\alpha$ -olefin the acid groups of which are esterified with an ethoxylated alcohol having a degree of ethoxylation of 1-45, hereinafter called esterified copolymer, is used to make aqueous peroxide emulsions with a small droplet size and a relatively low viscosity. With one exception where no anti-freeze was used at all, the emulsions contain methanol as an anti-freeze. The patent application suggests that surfactants as listed in EP-A-0 106 627 may be employed as a standard additive. However, EP-A-0

15 106 627 discloses a tremendously wide range of surfactants. For instance, they include anionic and cationic as well as nonionic surfactants. Furthermore, some are sugar based, some are polymeric, some are ethoxylated, etcetera. Even the preferred surfactants cover a wide range of products.

20

25 As stated above, the prior art emulsions show a small droplet size and a relatively low viscosity. However, following these references we were not able to develop peroxide emulsions that were completely satisfactory. More particularly, only methanol could be used as an anti-freeze, while also various physical properties could not be balanced properly, sometimes even resulting in unsafe formulations. Therefore, there is a need for new peroxide emulsions that show

30 more balanced physical properties and are more tolerant in respect of the anti-freeze agent that can be used. Accordingly, an aqueous peroxide emulsion with



the following properties is desired:

- low viscosity, preferably lower than 400 mPa.s,
- small peroxide droplet size, preferably the d50 is less than 2  $\mu\text{m}$ ,
- narrow droplet size distribution, preferably the d99 is less than 9  $\mu\text{m}$ ,
- 5 - a stable droplet size distribution over time, preferably for six months,
- no phase separation during storage,
- no formation of hazardous layers upon heating, and
- optionally containing anti-freeze agents, being methanol or other anti-freeze agents.

10

The emulsions according to the invention fulfill most, if not all, of these requirements. They are characterized in that the emulsifier system further comprises an ethoxylated fatty alcohol with an HLB value greater than 16.

15

It is noted that ethoxylated fatty alcohols have been used to produce aqueous peroxide suspensions, as is disclosed, for instance, in EP-A-0 517 290. However, the emulsifier systems as described in this patent application for peroxide suspensions are not suitable for the production of acceptable emulsions of peroxides. More specifically, they result in emulsions that are

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either too viscous or unsafe.

25

Furthermore, it is noted that the aqueous peroxide emulsions as described herein are limited to emulsions that remain liquid at the recommended storage temperature of the peroxide being emulsified. For peroxides that need refrigerated storage, this means that the emulsions according to the invention are liquids at temperatures as low as  $-20^{\circ}\text{C}$ .

30

The peroxides that can be formulated according to the invention can be of any conventional type. However, the emulsions are preferably those of peroxyesters, peroxydicarbonates, peroxycarbonates, diacyl peroxides, peracids or combinations thereof. The invention was proven to be pre-eminently suitable for emulsions of peresters and peroxydicarbonates. Examples of

suitable peroxides include: diisobutanoyl peroxide, 2,2-bis(2,2-dimethylpropanoylperoxy)-4-methyl pentane,  $\alpha$ -cumyl peroxyneodecanoate, 4-hydroxy-2-methylpentyl peroxyneodecanoate, 2-(2,2-dimethylpropanoylperoxy)-2-(2-ethylhexanoylperoxy)-4-methyl pentane, 2,4,4-trimethylpentyl-2

5 peroxyneodecanoate, tert-amyl peroxyneodecanoate, bis(2-ethylhexyl) peroxydicarbonate, tert-butyl peroxyneodecanoate, dibutyl peroxydicarbonate, di-sec-butyl peroxydicarbonate, diisopropyl peroxydicarbonate, 4-hydroxy-2-methylpentyl peroxypivalate, tert-amyl peroxypivalate, tert-butyl peroxypivalate, 2,2-bis(2-ethylhexanoylperoxy)-4-methyl pentane, bis(3,5,5-trimethylhexanoyl)

10 peroxide, 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane, isopropyl peracid, 4-hydroxy-2-methylpentyl peroxy-2-ethylhexanoate, tert-amyl peroxy-2-ethylhexanoate, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxydiethylacetate, tert-butyl peroxyisobutanoate, tert-butyl peroxy-3,5,5-trimethylhexanoate, 4-hydroxy-2-methylpentylperoxy isopropyl carbonate, tert-

15 butylperoxy isopropyl carbonate, tert-amylperoxy isopropyl carbonate, tert-butylperoxy 2-ethylhexyl carbonate, 4-hydroxy-2-methylpentylperoxy 2-ethylhexyl carbonate, tert-amylperoxy 2-ethylhexyl carbonate, 4-hydroxy-2-methylpentyl peroxyacetate, tert-butyl peroxyacetate, tert-amyl peroxyacetate, tert-butyl peroxybenzoate, tert-amyl peroxybenzoate, 4-hydroxy-2-methylpentyl

20 peroxybenzoate, cyclic methyl ethyl ketone peroxide (e.g. Trigonox® 301 ex Akzo Nobel), cyclic methyl isobutyl ketone peroxide, cyclic methyl isopropyl ketone peroxide, 2,5-dimethyl-2,5-di(tert-butylperoxy) hexane, and di-tert-butyl peroxide. The amount of organic peroxide in the aqueous emulsion is between 15 and 70% by weight, based on the weight of the emulsion. More preferably,

25 there is 40-65% by weight of peroxide and most preferably, 50-65% by weight of peroxide is present. At concentrations of less than 15% by weight the cost of transportation of the peroxide becomes very high and at concentrations above 70% by weight the products cannot be easily handled and often become intrinsically unsafe. However, emulsions containing 15-40% by weight of

30 peroxide may be necessary if the peroxide cannot be handled in a concentrated form. More specifically, when a peroxide can only be produced as a dilute solution in a phlegmatizer, which is often the case for highly reactive peroxides

with a one hour half-life temperature below 60°C when measured in chlorobenzene, then only such a dilution can be converted to an emulsion. Because the amount of organic material (to which the phlegmatizer belongs) that can be emulsified is limited to, typically, 70% by weight or less, the amount  
5 of peroxide in the emulsion will be reduced accordingly.

The esterified copolymer is a copolymer of at least one  $\alpha,\beta$ -unsaturated dicarboxylic acid ester and at least one  $C_{8-24}$   $\alpha$ -olefin, said dicarboxylic acid component of said copolymer being esterified by at least one ethoxylated  
10 alcohol having a degree of ethoxylation of 1-45. The esterified copolymers generally have a molar ratio of  $\alpha$ -olefin to  $\alpha,\beta$ -unsaturated dicarboxylic acid ester of 0.5-4. Such copolymers, and the methods for their manufacture, are described in detail in U.S. patent 4,931,197, which description is hereby incorporated by reference. The copolymers of  $\alpha$ -olefin and dicarboxylic acid  
15 ester may be esterified by at least one ethoxylated alcohol having a degree of ethoxylation of 1-45. Such ethoxylated alcohols may also contain propoxy groups. If in addition to the ethoxy groups in the ethoxylated alcohol propoxy groups are present, it is preferred that the degree of propoxylation be 1-10,. An example of a suitable esterified copolymer is Dapral® GE202 as obtainable  
20 from Akzo Nobel. The esterified copolymer is typically used in an amount of from 0.05 to 20% by weight, based on the amount of peroxide. Preferably, it is used in an amount of from 0.10 to 15% by weight, while an amount of from 0.20 to 10% by weight, all based on the amount of emulsified peroxide, is most preferred.

25

The ethoxylated fatty alcohol with an HLB value greater than 16 which forms the other essential part of the emulsifier system according to the invention can be selected from the conventional ethoxylated fatty alcohols with said HLB value. Said HLB value is the HLB-value as generally accepted in the industry, being  
30 the hydrophilic-lipophilic balance as worked out by the Atlas Powder Company and published in "The Atlas HLB-System, a time saving guide to emulsifier

- selection" in 1963. Examples of suitable compounds include ethoxylated lauryl alcohol, e.g., with a degree of ethoxylation of 23, having an HLB-value of 16.9, and obtainable from ICI as Brij® 35, ethoxylated dodecyl alcohol, such as Remcopal® 20, ethoxylated myristyl alcohol, ethoxylated cetyl alcohol, 5 ethoxylated oleyl alcohol, ethoxylated mixtures of alcohols, such as Ethylan® CO35 which is the ethoxylated product from a mixture of palmitic and oleyl alcohol, ethoxylated alcohols derived from coconut oil, palmitic acid, and/or tallow, and ethoxylated stearyl alcohol, e.g., with a degree of ethoxylation of 80 with an HLB-value of 18.5, and obtainable from Akzo Nobel as Berol® 08.
- 10 Preferably, the ethoxylated fatty alcohol has an HLB-value greater than 16.5, more preferably greater than 17.0. The ethoxylated fatty alcohol is typically used in an amount of 0.02 to 15 % by weight, based on the amount of emulsified peroxide. More preferably, it is used in an amount of 0.05 to 10% by weight, most preferably 0.1 to 7.5% by weight, all based on the weight of the
- 15 emulsified peroxide. Although the amount of ethoxylated fatty alcohol can be chosen independently from the amount of esterified copolymer used, it is preferred to use a total of both components in an amount of at least 0.5% by weight, more preferably 0.75% by weight, based on the weight of the emulsified peroxide. The HLB of the ethoxylated fatty alcohol in practice will be below 30.
- 20 Preferably it is below 25 and even more preferably below 22.

- Although it is preferred that the emulsifier system as used in the emulsions according to the invention consists essentially of the esterified copolymer and the ethoxylated fatty alcohol, it is possible to also use further nonionic
- 25 surfactants in the formulation. More particularly, one may opt to use some further nonionic surfactant to improve, for instance, the performance of the peroxide emulsion in the process wherein it is used. However, if so, it is preferred to use a combination of surfactants where the combined HLB-value, on a weight average basis, is greater than 16, preferably greater than 16.5, and
- 30 most preferably greater than 17.0.

Especially when peroxides are used that require refrigerated storage, see for

instance in the brochure "Initiators for high polymers" published by Akzo Nobel with code 10737, which peroxides include diisobutanoyl peroxide,  $\alpha$ -cumyl peroxyneodecanoate, 2,4,4-trimethylpentyl-2 peroxyneodecanoate, tert-amyl peroxyneodecanoate, bis(2-ethylhexyl) peroxydicarbonate, tert-butyl peroxyneodecanoate, dibutyl peroxydicarbonate, di-sec-butyl peroxydicarbonate, diisopropyl peroxydicarbonate, tert-amyl peroxy-pivalate, tert-butyl peroxy-pivalate, bis(3,5,5-trimethylhexanoyl) peroxide, 2,5-bis(2-ethylhexanoylperoxy)-2,5-dimethylhexane, tert-amyl peroxy-2-ethylhexanoate, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxydiethylacetate, and tert-butyl peroxyisobutanoate, it is preferred to use an anti-freeze agent in the aqueous peroxide emulsion. Depending on the use of the peroxide emulsion, it may be preferred to use an anti-freeze agent other than methanol. Conventional peroxide emulsions often contain methanol, since this agent typically does not influence the viscosity of the final emulsion too much. It was observed that the emulsions according to the invention are far more tolerant as to the type of anti-freeze agent that is used and the effect thereof on the final viscosity. The amount and type of anti-freeze to be used depends on the nature and amount of peroxide that is being formulated as well as on the type of anti-freeze, or mixture of anti-freezes, that is used. However, the inventors found it convenient to adjust the amount of anti-freeze agent(s) such that the mixture of just the anti-freeze and water that is used to form the emulsion shows a freezing point below the storage temperature necessary for handling the peroxide. A skilled person will have no difficulties in balancing the ratio of water to anti-freeze agent such that a certain desired freezing temperature is reached. Typically, the amount of anti-freeze agent used in the emulsion will be lower than the amount of water. The anti-freeze agents include, but are not limited to, salts, alcohols, including glycols, and other agents disrupting the hydrogen bridging structure of freezing water. Preferably, use is made of methanol, ethanol, isopropanol, ethylene glycol, propylene glycol, glycerol, and/or mixtures thereof, since it is known that such compounds will have hardly any effect on the polymerization process in which the emulsions are used later on.

The viscosity of the final emulsion preferably is such that it is easy to pour and/or pump. Typically, this means that the viscosity when measured according to Erichsen using an Erichsen model 332 viscometer with a shear rate of about  $200 \text{ s}^{-1}$ , at a temperature of  $0^\circ\text{C}$ , is below  $300 \text{ mPa.s}$ . More preferably, the Erichsen viscosity of the emulsion is between  $10$  and  $200 \text{ mPa.s}$  at  $0^\circ\text{C}$ . Most preferably, the viscosity of the emulsion is between  $20$  and  $100 \text{ mPa.s}$ . At this viscosity it is preferred that the  $d_{50}$  of the peroxide droplet distribution, when measured with a Malvern® Easy Sizer, is from  $0.1$  to  $2.0 \mu\text{m}$  while the  $d_{99}$  is from  $0.5$  to  $9.0 \mu\text{m}$ , preferably from  $0.5$  to  $5.0 \mu\text{m}$ . Also, the preferred emulsions retain these properties during storage. Such features are obtainable by using the emulsifier system according to the invention and using a high-shear mixer to finely divide the peroxide in the aqueous phase. Such high-shear mixtures can be any of the conventional ones and include ultrasonic mixers, homogenizers, perl-mills, high-speed rotor-stator mixers, e.g. Ultra-Turrax®, Dispax®, and the like. The final droplet size of the peroxide is influenced, *inter alia*, by the amount and composition of the emulsifier system that is used and the stirring energy that is used. However, with the information as presented herein, the skilled person will have no difficulty producing the preferred peroxide emulsions.

In order for the peroxide emulsions to be safe, it is essential that they do not show separation into one or more hazardous layers upon heating. Preferably, the peroxide in the emulsion decomposes gradually and in a controlled fashion. Typically, the heat of evaporation of the water of the emulsion and the volatile decomposition products that are formed suffice to remove the heat of decomposition.

For ease of reference; a peroxide emulsion is considered to be unsafe when upon heating sample of the emulsion, to a temperature  $30^\circ\text{C}$  higher than the self-accelerating decomposition temperature (SADT) of the most concentrated commercially acceptable dilution of the peroxide in isododecane in a  $25 \text{ kg}$  container (see, for instance, the brochure of Akzo Nobel titled "Initiators for high polymers" with code 10737 as available from Akzo Nobel Chemicals), a layer is

formed with an active oxygen content of more than 1% by weight. In order to minimize safety-risks, such a test is to be performed with appropriate shielding of operators. In our laboratories we conducted this test using a thermostatted vessel of 200 ml, with a diameter of 3.2 cm, and containing about 190 ml of the emulsion to be evaluated.

Further, other additives as typically used when making emulsions of peroxides may be incorporated into the emulsion. Such additives include pH-adjusting agents such as phosphate buffers, sequestering agents, and, if desired, biocides, e.g. fungicides, etc. The concentration of these additives will depend on the desired effect and the other ingredients in the suspension.

The peroxide emulsions can be used in various polymerization reactions, including the curing of unsaturated polyester resins, and polymer modification reactions, including degradation, cross-linking, and grafting reactions. They are, however, pre-eminently suited for use in a polymerization process as (one of) the polymerization initiator(s) in the polymerization of vinyl chloride alone or in admixture with up to 40% by weight of one or more ethylenically unsaturated monomers copolymerizable therewith, oligomers and (co)polymers of the aforementioned monomers, and mixtures of two or more of these monomers, oligomers, and polymers. The use of the emulsions in such processes is detailed below.

The preferred polymerizable monomers for the present polymerization process include vinyl halides, particularly vinyl chloride, and ethylenically unsaturated monomers having at least one terminal unsaturated group. Examples of such ethylenically unsaturated monomers include esters of acrylic acid, such as methyl acrylate, ethyl acrylate, butyl acrylate, octyl acrylate, cyanoethyl acrylate, and the like, esters of methacrylic acid, such as methyl methacrylate, butyl methacrylate, and the like, styrene and styrene derivatives including  $\alpha$ -methylstyrene, vinyl toluene, chlorostyrene, and the like, acrylonitrile, ethyl vinyl benzene, vinyl acetate, vinyl naphthalene, etc., and di-olefins including, but not

limited to, butadiene, isoprene, chloroprene, and the like, and other ethylenically unsaturated monomers known to those of ordinary skill in the art.

In addition, oligomers and polymers made from one or more of the above-identified monomers may also be reacted with other monomers, polymers or oligomers in the present polymerization process. Of course, mixtures of two or more of the polymerizable materials can be used. In all cases there will be at least 60% of vinyl chloride monomer, oligomer or polymer in the polymerizable mixture.

Generally, a polymerizable composition comprises 0.01-6.0% by weight of one or more peroxides, based on the monomers, as an initiator and when vinyl chloride is polymerized alone, preferably there will be 0.01-0.5% by weight of the peroxide, based on the monomer. If one or more of the peroxides are in the form of an emulsion according to the invention, the amount of the emulsion is to be chosen such that the indicated amount of pure peroxide is supplied. In the case of use as a chain transfer agent, e.g. when a peracid is employed, typically a concentration of between 0.01 and 10.0% by weight of pure chain transfer agent is used, based on the polymerizable materials. Preferably, from 0.05 to 1% by weight of these chain transfer agents is used.

A significant advantage of the present process for the polymerization of vinyl chloride is that the use of the emulsions of the present invention leads to greater flexibility in the polymerization process itself. More particularly, in conventional vinyl chloride polymerization processes the peroxide composition must be added to the monomer before the mixture is brought to the polymerization temperature in order to avoid adverse effects, such as increased fish-eye levels, on the properties of the resultant polymer. However, in the process of the present invention, the polymerization initiator emulsion may be added to the vinyl chloride monomer after it is heated to the polymerization temperature or may even be dosed stepwise or gradually during the polymerization reaction. These features provide greater flexibility in the polymerization process as well as a means of gaining better control over the



process and the products of the process.

The polymerization process of the present invention typically is a suspension polymerization process in which an aqueous dispersion of vinyl chloride monomer and the polymerization initiator are heated to cause polymerization of the monomer as a result of free radical decomposition of the polymerization initiator. The polymerization conditions employed are the conventional conditions for vinyl chloride monomer polymerization. For a detailed description of the process conditions, as well as the types of monomers which can be polymerized by this method, reference may be made to US 3,825,509, which is incorporated herewith by reference.

The present process, however, may differ slightly from that of US 3,825,509 in that it is not necessary to add the ingredients to the polymerization reactor in the order of water, dispersant, polymerization initiator, and, finally, monomer. While this conventional methodology is within the scope of the present invention, the present invention also encompasses reactions where the water, the dispersing agent, and the monomers are added to the reactor and heated to the polymerization temperature prior to the introduction of the polymerization initiator. In such reactions the polymerization initiator is added all at once, gradually or stepwise during the polymerization process.

Furthermore, it was proven that the peroxide emulsions according to the invention were useful in the suspension polymerization of predominantly styrene, as well as in the modification of polypropylene (PP). In respect of the latter use, it will depend on the type of peroxide emulsion and the modification process whether degradation or cross-linking reactions of PP will dominate.

In a final aspect, the present invention also relates to vinyl chloride-containing polymers produced by the process of the present invention. These polymers exhibit different properties from other vinyl chloride-containing polymers, including better electrical properties, lower fish-eye levels, and, in some

instances, improved polymer morphology, such as porosity.

The invention is further illustrated by the following examples.

#### 5 Examples 1 and 2 and Comparative Examples A and B

In Examples 1 and A an emulsion is produced containing:

- 60.0% by weight (%w/w) of bis(2-ethylhexyl) peroxydicarbonate,
- 2.0%w/w of Dapral GE 202,
- optionally Berol 08 (see table), and
- 10 - the balance being a mixture of water/methanol with a freezing point of – 20°C.

In Examples 2 and B an emulsion is produced containing:

- 50.0%w/w of 2,4,4-trimethylpentyl-2 peroxyneodecanoate,
- 0.1 or 0.4%w/w of Dapral GE 202 (see table),
- 15 - optionally Berol 08 (see table), and
- the balance being a mixture of water/methanol with a freezing point of -20°C.

All indicated amounts are based on the weight of the final emulsion. A "+" under the heading "safety" means that the emulsion did not show phase separation when kept for 8 hours at a temperature of 30°C above the SADT, while a "-" means that phase separation was observed and that consequently, such emulsions are unsafe.

Example	1	A	2	B
Dapral GE 202 (%w/w)	2	2	0.1	0.4
Berol 08 (%w/w)	0.5	0	0.3	0
Viscosity (mPa.s)	247	75	75	70
d50 (%w/w)	1.4	2.1	1.7	3.1
d99 (%w/w)	2.6	4.4	3.3	7.0
Safety	+	-	+	-

These results show that emulsions of at least two different types of peroxides

can be produced, that it is essential to use a nonionic in conjunction with the esterified copolymer, and that the concentration of the emulsifier system can vary between wide ranges while still leading to the desired effect.

5

#### Example 3 and Comparative Examples C and D

An emulsion containing 50%w/w of 2,4,4-trimethylpentyl-2-peroxyneodecanoate and 3%w/w of an emulsifier system (see table), the remainder being a mixture of water/methanol with a freezing point of  $-20^{\circ}\text{C}$ , was used in the polymerization of VCM in a 1l. stainless steel Büchi autoclave with 3-bladed stirrer, baffle, and temperature sensor. The polymerization recipe was as follows:

10

VCM	260 g
H <sub>2</sub> O	520 g
15 KP-08 (PVA)	0.39 g
Peroxyester emulsion	0.26 g (0.05 %w/w of pure peroxide on VCM)
Na <sub>2</sub> HPO <sub>4</sub>	0.1 g
NaH <sub>2</sub> PO <sub>4</sub>	0.1 g

20

The PVA was dissolved in the water and the phosphate buffer was added. The reactor was evacuated and flushed with N<sub>2</sub> four times (at room temperature). While stirring at 735 rpm, VCM was added. Subsequently, the reactor was heated to  $53.5^{\circ}\text{C}$  in 25 minutes. Then the initiator emulsion was added by injection through a septum. The polymerization was stopped after 480 minutes

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by venting off unreacted VCM and cooling. The PVC that was formed was filtered, washed with H<sub>2</sub>O, and dried overnight at  $30^{\circ}\text{C}$  in an air oven and analyzed. The fish-eye number of the resulting PVC was measured as described by O. Leachs in *Kunststoffe*, Vol. 50(4), 1960, pp 227-234.

Example	3	C	D
Dapral GE202 (%w/w)	2.5	0	3.0
Berol 08 (%w/w)	0.5	3.0	0
Fish eyes (dm <sup>-2</sup> )	10	20	1300

This shows that the emulsions of the invention result in PVC with very low fish-eye numbers.

#### 5 Examples 4 and 5 and Comparative Examples E-J

Emulsions were prepared containing:

- 50.0% by weight (%w/w) of tert-butyl peroxyneodecanoate,
- 2.5%w/w of Dapral GE 202,
- 10 - 0.5%w/w of a nonionic surfactant (see table), and
- the balance being a mixture of water/methanol with a freezing point of -20°C.

Example	4	5	E	F	G	H	I	J
Surfactant	EFO H 1	EFO H 2	EFO H 3	EFO H 4	EFO H 5	ESM	ECG	EFA
HLB value	16.0	17.2	11.5	13.5	15.4	16.7	18.0	18.0
Viscosity (mPa.s)	50	55	60	60	60	55	55	60
d50 (%w/w)	1.2	1.3	1.0	0.8	1.2	1.4	0.9	1.1
d99 (%w/w)	12.2	5.5	3.9	4.5	5.2	3.6	2.9	4.5
Safety	+	+	-	-	-	-	-	-

EFOH 1 = Remcopal® 20 ex CECA = ethoxylated fatty alcohol

EFOH 2 = Ethylan® CO 35 ex Akcros = ethoxylated fatty alcohol

15 EFOH 3 = Berol® 087 ex Akzo Nobel = ethoxylated fatty alcohol

EFOH 4 = Berol® 185 ex Akzo Nobel = ethoxylated fatty alcohol

EFOH 5 = Ethylan® R ex Akcros = ethoxylated fatty alcohol

ESM = Tween® 20 ex ICI = ethoxylated sorbitan monolaurate

ECG = Softigen® 767 ex Hüls = ethoxylated capril/caprilic glyceride

EFA = Cithrol® 10 ML ex Croda = ethoxylated fatty acid

These results show that the emulsifier system according to the invention must contain an ethoxylated fatty alcohol of the appropriate HLB-value.

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#### Examples 6 and 7 and Comparative Examples K and L

Emulsions were prepared containing:

- 50.0% by weight (%w/w) of 2,4,4-trimethylpentyl-2-peroxyneodecanoate,
- 10 - 2.7%w/w of Dapral GE 202 in Examples 6 and 7 and 3.0%w/w in Examples K and L,
- 0.3%w/w of Berol 08 in Examples 6 and 7 and none in Examples K and L, and
- the balance being a mixture of water and anti-freeze agent according to the
- 15 table with a freezing point of  $-20^{\circ}\text{C}$ .

Example	6	7	K	L
Anti-freeze agent	Methanol	ethanol	Methanol	ethanol
d50	1.6	0.6	1.3	39.9
d99	3.0	1.5	3.3	110.6
Safety	+	+	-	n.r.
Viscosity	80	151	n.r.	n.r.

n.r. = not relevant

These results show the higher tolerance of the emulsions according to the invention in respect of the anti-freeze agent that can be used.

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#### Examples 8, 9 and 10

For Examples 8 and 9 emulsions were prepared containing:

- 25 - 50.0% by weight (%w/w) of bis(2-ethylhexyl) peroxydicarbonate,

- 2.0%w/w of Dapral GE 202,
- 0.5%w/w of Berol 08, and
- the balance being a mixture of water and anti-freeze agent according to the table with a freezing point of  $-20^{\circ}\text{C}$ .

5 In Example 8 ethylene glycol was used as the anti-freeze agent, whereas in Example 9 propylene glycol was used. Both emulsions were acceptable from a safety and use point of view.

In Example 10, Example 1 was repeated, except that ethanol was substituted for the methanol. Also this emulsion was acceptable from a safety and use point of view.

#### Comparative Examples M-P

Emulsions were prepared containing:

- 50.0% by weight (%w/w) of 2,4,4-trimethylpentyl-2-peroxyneodecanoate,
- 15 - 3%w/w of an emulsifier system, optionally containing Berol 08, but comprising Unitika UMR10M, a PVA, instead of the esterified copolymer, and
- the balance being a mixture of water and anti-freeze agent according to the table with a freezing point of  $-20^{\circ}\text{C}$ .

20 The following results were obtained.

Example	M	N	O	P
Unitika UMR10M (%w/w)	3	2	1	0
Berol 08 (%w/w)	0	1	2	3
Viscosity (mPa.s)	440	430	330	330

Handling of these emulsions was troublesome due to the high viscosity, especially when compared to the emulsion of Example 6 above.

#### 25 Comparative Example Q

An emulsion was made containing 50%w/w of  $\alpha$ -cumyl peroxyneodecanoate, 1%w/w Unitika UMR10M (PVA) ex Unitika and 1%w/w Alcotex 552P (PVA) ex

16.

Harco and 0.15%w/w Berol 08. The viscosity of the resulting emulsion was about 950 mPa.s and unacceptable.

PCT/EP00/00003

## Claims

1. Aqueous peroxide emulsion, optionally containing anti-freeze and/or further additives, which contains a specific emulsifier system comprising a  
5 copolymer of an  $\alpha,\beta$ -unsaturated dicarboxylic acid and a  $C_{8-24}$   $\alpha$ -olefin the acid groups of which are esterified with an ethoxylated alcohol having a degree of ethoxylation of 1-45, characterized in that the emulsifier system further comprises an ethoxylated fatty alcohol with an HLB-value greater than 16.  
10
2. Emulsion according to claim 1 wherein the emulsifier system consists essentially of the copolymer of an  $\alpha,\beta$ -unsaturated dicarboxylic acid and a  
15  $C_{8-24}$   $\alpha$ -olefin the acid groups of which are esterified with an ethoxylated alcohol having a degree of ethoxylation of 1-45 and the ethoxylated fatty alcohol.
3. Emulsion according to claim 1 or 2 wherein the peroxide is selected from the group consisting of peroxyesters, peroxydicarbonates, peroxycarbonates, diacyl peroxides, peroxides, and combinations thereof,  
20 and in which said peroxide is present in an amount of 30-70% by weight, based on the weight of the emulsion.
4. Emulsion according to claim 3 comprising one or more peroxides which require refrigerated storage and are present in an amount of 40-65% by  
25 weight, preferably 50-65% by weight, based on the weight of the emulsion.
5. Emulsion according to claim 4 further comprising an anti-freeze selected from the group consisting of methanol, ethanol, isopropanol, ethylene  
30 glycol, propylene glycol, and glycerol.



6. Emulsion according to any one of the preceding claims wherein the copolymer is present in an amount of 0.05 to 20% by weight and the ethoxylated fatty alcohol is present in an amount of 0.02-15% by weight, while the total weight of both compounds is at least 0.5% by weight, all based on the weight of the peroxide in said emulsion.
7. Emulsion according to claim 6 wherein the copolymer is present in an amount of 0.1-15% by weight, preferably 0.2-10% by weight, based on the weight of the peroxide.
8. Emulsion according to any one of the preceding claims wherein the HLB value of the ethoxylated fatty alcohol is greater than 16.5, preferably greater than 17.0.
9. Emulsion according to any one of the preceding claims wherein the droplet size of the emulsion, when measured using a Malvern Easy Sizer, is characterized by a d50 of 0.1-2.0  $\mu\text{m}$  and a d99 of 0.5-9.0  $\mu\text{m}$ .
10. Emulsion according to any one of the preceding claims with a viscosity of 10-300 mPa.s.
11. Use of an emulsion according to any one of the preceding claims in a polymerization or polymer modification reaction, preferably a reaction involving the polymerization of at least vinyl chloride.
12. Polyvinyl chloride obtainable by a process involving the reaction of at least vinyl chloride monomer and a peroxide that was used in the form of an emulsion according to any one of claims 1-10.

## DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: **AQUEOUS PEROXIDE EMULSIONS**

the specification of which:

☒ was filed on 6 January 2000 as Appln. Ser. No. PCT/EP00/00003

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. All factual statements made in the specification of my own knowledge are true and all factual statements made on information and belief are believed to be true.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, Sec. 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, Sec. 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

			<u>Priority Claimed</u>
<u>99200066.1</u>	<u>EUROPE</u>	<u>12 JANUARY 1999</u>	<u>X</u> Yes ___ No
(Number)	(Country)	(Day/Month/Year)	
<hr/>			___ Yes ___ No
(Number)	(Country)	(Day/Month/Year)	

I hereby claim the benefit under Title 35, United States Code § 119 of any provisional application(s) listed below:

Appln., Ser. No.	Country	Day/Month Year
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I hereby claim the benefit under Title 35, United States Code, Sec. 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, Sec. 112.

(Appln. Ser. No.) (Filing Date) (Status: patented, pending, abandoned)

**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following as my attorneys of record, with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent Office:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Sec. 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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